

PATENT SPECIFICATION

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(54) CHEMICAL REACTORS

(71) We, MONTEDISON S.P.A., a Body Corporate organised and existing under the laws of Italy, of 31 Foro Buonaparte, Milan, Italy, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

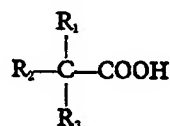
The invention relates to chemical reactors which have proved particularly but not exclusively suitable for polymerizing vinyl monomers.

The invention provides a chemical reactor in the form of a closed loop comprising a number of sections detachably connected in sequence, the said sections comprising a pump for circulating reaction medium around the loop, a delivery section having from 5 to 30% of the volume of the reactor, a central section shorter than the delivery section, and a further section leading back to the pump. The delivery section and the further section may be of substantially the same length and parallel to each other. Each may be more than 5 times as long as the central section. The delivery section preferably has 15% of the total volume of the reactor.

A reactor according to the invention can cheaply and inexpensively be constructed from pipe sections having relatively low diameter and consequently of relatively small thickness. This leads to low operating costs due to less power requirement for the circulation of the reaction mass.

Reactors according to the invention have proved particularly suitable for the homo- and copolymerization of unsaturated esters or vinyl monomers in emulsion and solution from liquid or gaseous monomers. Vinyl esters such as vinyl acetate, propionate, versate, butyrate, or benzoate; or methyl, ethyl, butyl or octyl acrylate or maleate or styrene may be copolymerized with ethylenically unsaturated gaseous comonomers such as vinyl chloride,

ethylene, propylene, 1-butene, 1-hexene or a mixture of two or more olefins having from 2 to 6 carbon atoms in the molecule. Vinyl versate is a mixture of vinyl esters of acids having 10 carbon atoms, each of them having the following structure:



wherein R_1 , R_2 , R_3 are linear alkyl groups, at least one of which is methyl. (Vinyl versate is sold under the Trade Mark "Veova 10").

Very advantageous is the preparation of vinyl acetate-ethylene copolymers containing from 5 to 50% by weight of ethylene. The preparation of vinyl acetate-ethylene-vinyl chloride terpolymers containing from 5 to 40% by weight of ethylene and from 5 to 40% by weight of vinyl chloride is also of interest due to the properties of the products obtained.

Water-soluble or oil-soluble free-radical initiators may be employed as catalysts. In particular, when aqueous dispersions of polymers are to be prepared, ionic or non-ionic surface-active agents may be used, either individually or in combination with one another, as emulsifiers. Water-soluble natural and synthetic products may be used as protecting colloids and thickening agents.

For polymerisation in solution it is possible to use, as solvents, organic compounds capable of dissolving the monomers and possibly also the corresponding polymers, such as methanol, ethyl acetate, methyl acetate, acetic acid, acetone, trichloroethylene, toluene, benzene and tert.-butyl alcohol. For polymerization in suspension, dispersants and stabilizers may be employed.

The operating pressure may range from

1 to 300 kg/sq.cm. (gauge) depending upon the composition of the resin to be obtained. The reaction temperature may be from 15 to 150°C, preferably from 40 to 100°C, according to the polymerization technique and catalyst system employed. Reaction may be continuous or discontinuous.

A chemical reactor according to the invention is illustrated by way of example in the drawing: A reactor 3 in the overall form of an annular tube comprises in sequence a circulating pump 1 leading to the left into a delivery section having 15% of the volume of the whole reactor 3, a central section which appears at the top in the drawing and is shorter than the delivery section, and a further section to the right in the drawing leading back to the pump 1. Each of the sections is enclosed in the thermo-regulating jacket 2 so that its temperature can be controlled by means of fluid introduced into each jacket 2 at 6 and removed at 6'. The reactor 3 includes reagent inlets 5, 5' and discharge nozzles 4, 4'.

This reactor has been used for the polymerization of vinyl esters to give a good yield of products having good characteristics such as small particle diameter, high binding power for pigments, high water resistance in film form, and high viscosity.

The invention is illustrated by the following Examples.

Example 1

A closed loop, stainless steel, 36 litre reactor as in the drawing was fed with an initial polymerization reaction medium consisting of:

| | |
|---|----------|
| vinyl acetate | 3,296 g |
| water | 12,453 g |
| sodium dodecylbenzenesulphonate | 62 g |
| condensate of ethylene oxide with oleyl alcohol | 315 g |
| high viscosity hydroxyethyl cellulose | 157 g |
| potassium persulphate | 22 g |
| crystalline sodium acetate | 104 g |

After having discharged the gases from the reactor, ethylene was introduced up to a pressure of 20 kg/sq.cm. (gauge). The temperature of the mass was 90°C and the circulation rate of the fluid undergoing polymerization 2,500 litres per hour. The reactor was fed, by means of a constant-delivery proportioning pump, during four hours with:

| | |
|--|----------|
| vinyl acetate | 10,642 g |
| potassium persulphate in a 5% aqueous solution | 1,740 g |

The reaction was then conducted for a further 2 hours. During the whole reaction

period, make-up ethylene was fed as ethylene was consumed, so as to keep the operating pressure at the pre-established value. The product obtained exhibited the following characteristics:

Combined ethylene content:

| | | |
|---|--------|----|
| % by weight on the resin | 14 | |
| Brookfield RVT viscosity at 20°C, 20 r.p.m. cP | 4420 | |
| Film building min. temperature °C | +4 | 70 |
| average diameter of particles μ | 0.15 | |
| Per cent elongation at break of the film at 23°C and 50% relative humidity | 550 | 75 |
| Tensile strength of the film at 23°C and 50% relative humidity kg/sq.cm. | 23 | |
| whitening (after 2, 10, 25 minutes) of the film being immersed in water at 20°C | | 80 |
| T% (percent transmittancy of light of wavelength 650 millimicrons) | 0,0,10 | |

Example 2

A reactor as in Example 1 was fed with an initial polymerization medium consisting of:

| | | |
|--|---------|----|
| water | 7,662 g | |
| high water viscosity hydroxyethylcellulose | 183 g | 90 |
| sodium dodecylbenzenesulphonate | 72 g | |
| sodium acetate | 24 g | |

After having discharged the gases from the reactor, at a mass temperature of 80°C, the following reagents were introduced during two hours:

| | | |
|-----------------------|---------|-----|
| vinyl acetate | 9,900 g | |
| vinyl versatate | 4,241 g | |
| potassium persulphate | 71 g | 100 |
| sodium acetate | 94 g | |
| water | 6,422 g | |

An ageing period of one hour followed. During the whole process the operating pressure did not exceed 2 kg/sq.cm. (gauge). The product characteristics were:

| | | |
|---|-------|-----|
| Diameter of particles μ | 0.10 | |
| Brookfield RVT viscosity at 20°C 20 r.p.m. cP | 8500 | |
| Film building minimum temperature °C | 5 | 110 |
| Whitening (after 2, 10, 25 minutes) of the film being immersed in water at 20°C | | |
| T% | 0,0,5 | 115 |

Example 3

Example 1 was followed as regards the equipment, operating technique and reagents with the exception that it was operated at a

pressure of 35 kg/sq cm (gauge) and that, as third comonomer, vinyl chloride in partial replacement of vinyl acetate was employed in the following amounts:

| | | |
|---|----------------|----------|
| 5 | vinyl acetate | 13,570 g |
| | vinyl chloride | 4,523 g |

The product exhibited the following characteristics:

| | | |
|----|---|----------|
| 10 | Composition of the vinyl acetate-ethylene-vinyl chloride resin weight % | 60/20/20 |
| | Brookfield RVT viscosity at 2°C, 20 r.p.m. cP | 4500 |
| | Average diameter of particles μ | 0.14 |
| 15 | Whitening (after 2, 10, 25 minutes) of the film being immersed in water at 20°C | |
| | T% | 0,0,0 |

Example 4

20 The equipment described in Example 1 was fed with an initial polymerization medium consisting of:

| | | |
|----|--|----------|
| | water | 11,900 g |
| | vinyl acetate | 2,300 g |
| 25 | sodium dodecylbenzenesulphonate | 28 g |
| | condensate of ethylene oxide and oleyl alcohol | 254 g |
| 30 | polyvinyl alcohol (88% partial hydrolysis) | 588 g |
| | ammonium persulphate | 20 g |
| | sodium metabisulphite | 16 g |
| | crystalline sodium acetate | 81 g |

35 After having discharged the gases the reactor was fed with ethylene up to a pressure of 40 kg/sq.cm. (gauge). At a mass temperature of about 55°C and at a polymerization fluid circulating rate of 2,500 litres per hour, the following reagents were introduced into the reactor during four hours by means of constant-capacity proportioning pumps:

| | | |
|----|--|---------|
| | vinyl acetate | 9,300 g |
| | ammonium persulphate in a 4% aqueous solution | 1,500 g |
| 45 | sodium metabisulphite in a 3% aqueous solution | 1,200 g |

50 The reaction was then conducted for a further 2 hours. During the whole reaction period make-up ethylene was added as ethylene was consumed, so as to keep the operating pressure at the predetermined value. The product obtained exhibited the following characteristics:

| | | |
|----|---|--------|
| 55 | Combined ethylene content of the resin % by wt. | 20 |
| | Brookfield RVT viscosity at 20°C 20 r.p.m. cP | 20,000 |

Minimum film building temperature °C

-3

Bonding power: rigid PVC/ beech wood binding kg/4 cm (peel or stripping strength ASTM D903-49)

60

Example 5

65 An annular reactor like that in Example 1, with the only exception that the circulating pump is of the helical type, was fed with an initial polymerization medium made up of:

| | | | |
|--|--------------------------------------|----------|----|
| | water | 15,000 g | 70 |
| | polyvinyl alcohol | 30 g | |
| | low viscosity hydroxyethyl-cellulose | 45 g | |
| | vinyl acetate | 3,000 g | |
| | benzoyl peroxide (initiator) | 89 g | 75 |

The gases were discharged from the reactor and ethylene was introduced up to a pressure of 30 kg/sq.cm. (gauge). The reaction mass was thermoregulated at 75-80°C, and at this temperature, during four hours the remaining amount of vinyl acetate (10,000 g) and of initiator (100 g) was added, while make-up ethylene was discontinuously fed as ethylene was consumed. At the conclusion of a further reaction period of 1 hour and 30 minutes, the gases were discharged from the equipment and the product, consisting of small white spheroidal resin beads, having an ethylene content of 18% by weight, was discharged. The total time of the process was 6 hours.

Example 6

By employing the same method, equipment and charge amounts as in Example 5, with the exception that only vinyl acetate was used as a monomer, polymerization was conducted at a maximum pressure of 2 kg/sq.cm. (gauge) and beads were obtained. The total reaction time was 5 hours.

Example 7

100 The reactor was as in Example 1, except that the circulating pump was of the gear type. The reactor was fed with 20% by weight of a total charge consisting of:

| | | | |
|--|--------------------------------|----------|-----|
| | technical grade methyl acetate | 14,400 g | 105 |
| | vinyl acetate | 16,000 g | |
| | azo - bis - isobutyronitrile | 140 g | |

110 The gases were discharged from the equipment and ethylene was introduced up to a pressure of 40 kg/sq.cm. (gauge). The mass was heated to 70-80°C and at this temperature the reactor was fed, during 6 hours with the remaining amount of the charge. Make-up ethylene was discontinuously fed as ethylene was consumed. After a further 2

115

hours reaction, the product was discharged. The conversion of vinyl acetate into polymer was about 97%. The resin, isolated from the solution according to the usual techniques, contained 28 weight % of combined ethylene.

Example 8

By using the same process, equipment and charge amounts as in Example 7, with the sole exception of the recipe, which did not include ethylene, homopolymerization of vinyl acetate was conducted in solution at a pressure of 2 kg/sq.cm. (gauge). The total time of the reaction was 10 hours.

WHAT WE CLAIM IS:—

1. A chemical reactor in the form of a closed loop comprising a number of sections detachably connected in sequence, the said sections comprising a pump for circulating reaction medium around the loop, a delivery section having from 5 to 30% of the volume of the reactor, a central section shorter than the delivery section, and a further section leading back to the pump.
2. A chemical reactor according to claim 1 in which the delivery section has 15% of the total volume of the reactor.
3. A chemical reactor according to claim 1 or claim 2 in which the delivery section and the further section are each more than 5 times as long as the central section.
4. A chemical reactor as herein described with reference to the drawings.
5. A process of polymerizing an unsatur-

ated ester or vinyl monomer which is carried out in a chemical reactor according to any of the preceding claims.

6. A process according to claim 5 in which the polymerization is carried out in emulsion.

7. A process according to claim 5 in which the polymerization is carried out in solution.

8. A process according to any of claims 5 to 7 in which vinyl acetate is polymerized.

9. A process according to any of claims 5 to 8 in which a vinyl ester is copolymerized with a gaseous ethylenically unsaturated monomer.

10. A process of polymerizing a vinyl ester as described in any of Examples 1 to 6.

11. A process of polymerizing a vinyl ester as described in Example 7 or Example 8.

12. A polymer prepared by a process according to any of claims 5 to 11.

13. A vinyl acetate-ethylene copolymer according to claim 12 having an ethylene content of from 5 to 50% by weight.

14. A vinylacetate-ethylene-vinyl chloride terpolymer according to claim 12 the ethylene and vinyl chloride contents each being from 5 to 40% by weight.

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1482148

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

